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Professor Ki Hyun Yoon

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Yonsei University, Department of Ceramic Engineering
134 Shinchondong, Sudaemunku
Seoul 120-749
Korea (South)

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14. ABSTRACT

Recently, there has been considerable scientific and technological interest in ferroelectric thin films for numerous potential applications that utilize their dielectric, piezoelectric, pyroelectric and electro-optic properties.[i] Among them, lead zirconate titanate (PZT) and PZT-$Pb(Mg_{1/3}Nb_{2/3})O_3$ systems at compositions near their morphotrophic phase boundaries, have been investigated because of their excellent piezoelectric and dielectric properties for actuator and semiconducting memory devices.[ii,iii,iv] In this study, ferroelectric thin films with $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ ($0.3 \leq x \leq 0.9$) composition have been prepared by chemical soultion deposition with corresponding metal alkoxides partially stabilized with triethanolamine and acetylacetone. $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ thin films were deposited on Pt-coated substrate by spin–coating and crystallized at 700 °C in air. And then their dielectric properties were investigated

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[i] G. H. Haertling, "Ferroelectric Ceramics: History and Technology," *J. Am. Ceram. Soc.*, 82[4] 797-818 (1999).
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[iv] K. Sumi, H. Qiu, M. Shimada, and T. Nishiwaki, "Structure and Piezoelectric Properties of $0.9Pb(Zr,Ti)O_3$-$0.1Pb(Mg,Nb)O_3$ Films Prepared by Metalorganic Deposition Process," *Jpn. J. Appl. Phys.* 38, 886-89 (1999).

FINAL REPORT

Dielectric Properties of PMN-PT-PZ System

Ki Hyun Yoon
Research Institute of Advanced Materials
Yonsei University, Seoul 120-749
Korea

Dielectric Properties of PMN-PZ-PT System

Introduction

Recently, there has been considerable scientific and technological interest in ferroelectric thin films for numerous potential applications that utilize their dielectric, piezoelectric, pyroelectric and electro-optic properties.[1] Among them, lead zirconate titanate (PZT) and PZT-$Pb(Mg_{1/3}Nb_{2/3})O_3$ systems at compositions near their morphotrophic phase boundaries, have been investigated because of their excellent piezoelectric and dielectric properties for actuator and semiconducting memory devices.[2,3,4] In this study, ferroelectric thin films with $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ ($0.3 \leq x \leq 0.9$) composition have been prepared by chemical soultion deposition with corresponding metal alkoxides partially stabilized with triethanolamine and acetylacetone. $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ thin films were deposited on Pt-coated substrate by spin–coating and crystallized at 700 °C in air. And then their dielectric properties were investigated

Experimental Procedure

All of the starting solutions for $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ ($0.3 \leq x \leq 0.9$, hereafter PMN-PZT) were made to a concentration of 0.33 M. The detailed solution preparation method was similar to that used recently for PZ-BT chemical solution[5]. Schematic diagram of the experimental procedure for PZ and PT precursors are seen in Fig. 1. The 0.35 μm thick PMN-PZT films were produced by spin-coating on Pt(111)-passivated substrates at 2500 rpm for 30 sec. Each layer was pyrolyzed at 380 °C for 3 min and the deposited films were crystallized at 700 °C for 10 min. Structure and crystallinity of the films were characterized by XRD. The morphology and interfacial properties of films observed by SEM and AES. Low-field dielectric properties and high-field hysteresis properties were characterized by an impedance/gain phase analyzer and a modified computer-controlled Sawyer-Tower circuit, respectively. A fatigue test was conducted by applying bipolar square wave (V_{pp}=20 V, 100 kHz) from a function generator.

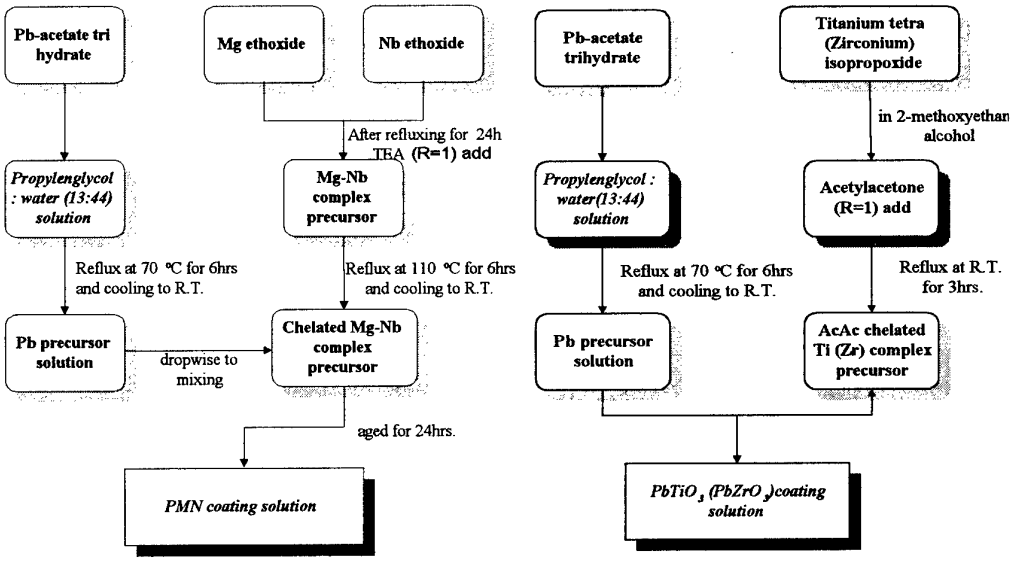

Figure 1 Schematic diagram for the chemical solution processing of PMN, PT, and PZ precursors.

Results and Discussion

Figure 2 shows XRD patterns of the PMN-PZT ($0.3 \leq x \leq 0.6$) thin films crystallized at 700 °C for 10 min. There are no secondary phases, such as the pyrochlore phase, and films were preferentially (111)-oriented. The grain size of thin films gradually decreased from ~250 nm to ~100 nm with increased Zr concentration (x). SEM analysis revealed that the microstructure was dense and rosette-free.

AES was performed to characterize the distribution of various elements through the film. As shown in Fig. 3, it represented little tendency for each element of thin film to diffuse into the platinum and form any complex alloy.

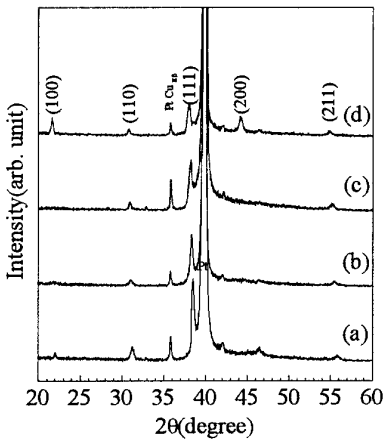

Figure 2 XRD patterns for the PMN-PZT films with various compositions, (a) x=0.3, (b) x=0.4, (c) x=0.5, and (d) x=0.6.

Figure 4 shows the small signal dielectric constant and dissipation factor as a function of frequency for 0.35 μm thick PMN-PZT films of various compositions.

The dielectric constant showed no dispersion with frequency up to about 100 kHz indicating that measured values were not masked by surface layer effects or electrode barrier effects in the measured frequency range. The dielectric constant of the thin films with various compositions showed a maximum value at $x = 0.5$ and were ~1500, as shown in Fig. 3. Through the composition range ($0.3 \leq x \leq 0.6$), dielectric loss was below 0.03, at 1 kHz.

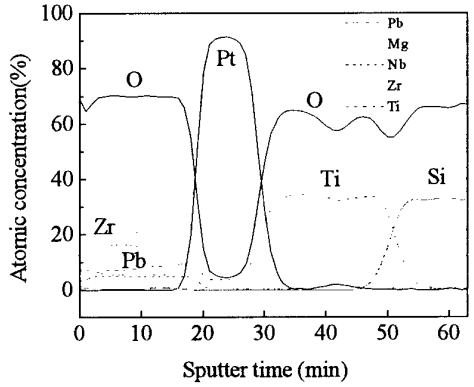

Figure 3. Auger depth profiles for the PMN-PZT thin film with composition of x = 0.5.

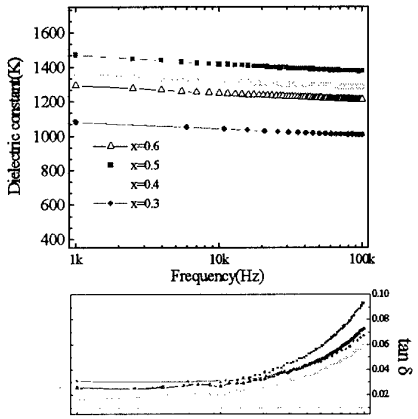

Figure 4. Frequency dependence of dielectric properties for the PMN-PZT films with various compositions.

Figure 5 shows polarization reversal properties for the thin films of various compositions. As shown in Fig. 4, the maximum value of remnant polarization (Pr) was found to be about 18 $\mu C/cm^2$ at x=0.5. The coercive field of the film (x=0.5) was about 41 kV/cm. The highest dielectric constant and remnant polarization observed in this study might be due to the nearby morphotrophic phase boundary in the thin film.

Figure 6 shows decay the remnant polarization for the thin film compositions of x=0.4 and x=0.5 as a function of number of cycles. In PZT films, charged oxygen vacancies are known to be highly mobile[6]. Brazier et al[7] have noted that the movement and redistribution of these charged species with field is responsible for the formation of a non-switching layer at the electrode. As far as loss of polarization is concerned, the PMN-PZT thin films can be sustained up to 74-82% of their initial remnant polarization values after 10^{10} cycles compared with that (about 50 % degradation after 10^9 cycles) of unmodified PZT thin films as reported elsewhere[8]. It appears that Mg^{+2}, and/or Nb^{+5} contribution in PZT decreases the drift mobility of oxygen vacancy, resulting in suppressed fatigue rate in the PMN-PZT films. It is quite well known in perovskite oxides such as barium titanate that some dopants in the position of Ti^{+4} can bind oxygen vacancies through dipolar interaction[9].

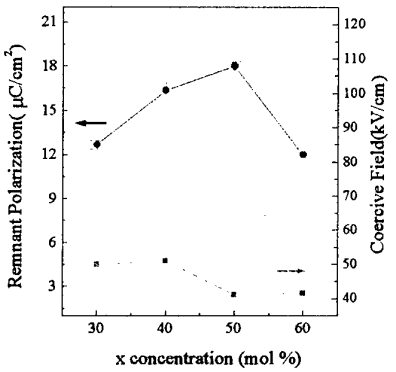

Figure 5. Variations of the remnant polarization (P_r) and coercive field (E_c) for the thin films as a function of Zr concentration.

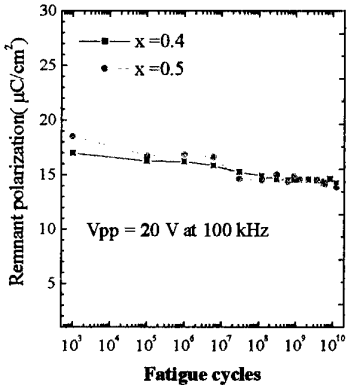

Figure 6. Decay in remnant polarization as a function of number of switching cycles for the films with composition of x=0.4 and 0.5.

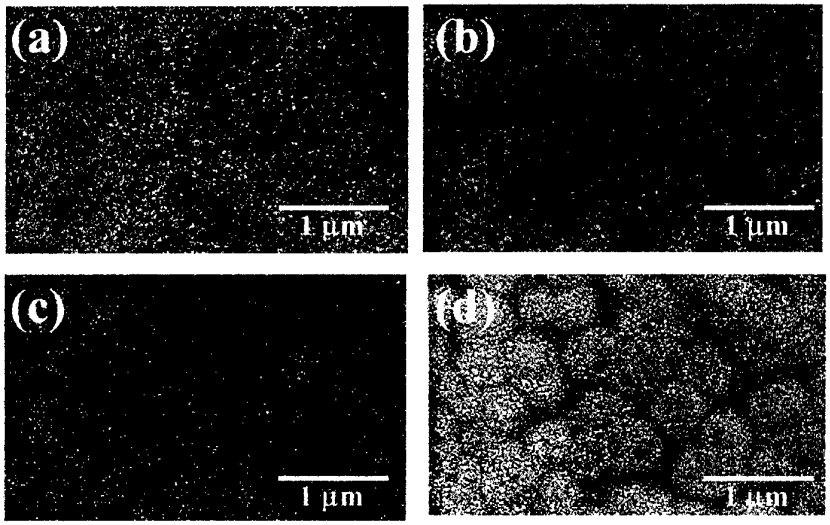

Figure 7. SEM photographs of 0.1PMN-0.9Pb(Zr_xTi_{1-x})O_3 films with various compositions, (a) x=0.6, (b) x=0.7, (c) x=0.8, and (d) x=0.9.

Compositionally, a majority of the studies have focused on compositions in close proximity to the rhombohedral/tetragonal morphotropic boundary (52/48)[3] because of their excellent dielectric and

piezoelectric properties in the morphotropic composition and those to the tetragonal side. While, softer hysteresis with lower coercive fields occurs for rhombohedral compositions. Therefore, rhombohedral compositions thus have the advantage of lower switching fields because the spontaneous directions are well defined compared to the near morphotropic composition in <111> direction.[10]

Figure 7 shows the microstructure of the surface of 0.1PMN-0.9Pb(Zr_xTi_{1-x})O_3 thin films with composition of x=0.6, 0.7, 0.8, and 0.9 (Fig. 7(a) to 7(d)). The films exhibited a dense microstructure with fine grain matrix. The grain size of thin films gradually decreased from ~150 nm to ~50 nm with increased Zr concentration (x). While, with decreasing content of x, the film shows less developed island microstructure compared to the clustered microstructure at the thin film composition of x=0.6 (Fig. 7(d)).

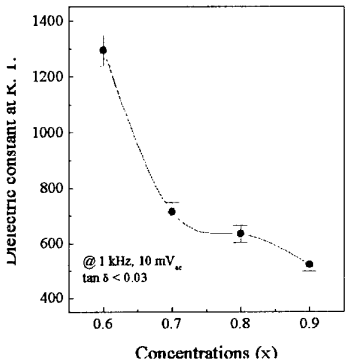

Figure 8. Room temperature dielectric constants for the PMN-PZT films as a function of x concentrations.

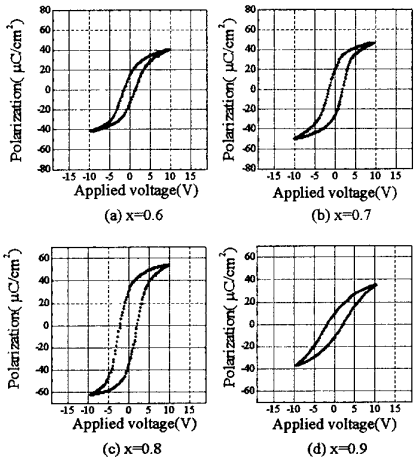

Figure 9. Hysteresis loops of the PMN-PZT films with various compositions, (a) x=0.6, (b) x=0.7, (c) x=0.8, and (d) x=0.9.

The room temperature dielectric constant of the thin films with various compositions (x = 0.6, 0.7, 0.8, and 0.9), linearly decreased with increasing content of x. The values of dielectric constants were ~1300, ~710, ~650, and ~500 at 1 kHz, respectively, as shown in Fig. 8.

The hysteresis loops of the PMN-PZT films of x = 0.6, 0.7, 0.8, and 0.9 were shown in Fig. 9(a), 9(b), 9(c), and 9(d), respectively. For the investigated compositions, it represented that well developed and fairly symmetric hysteresis loops with field. The remanent polarizations and coercive field of the films largely increased with increase of x and showed maximum values at the composition of x=0.8 in Fig. 9(c). The value of remanent polarization (P_r) and coercive field were ~28 μC/cm², 57 kV/cm, respectively, at the composition of x = 0.8.

Conclusion

0.1Pb($Mg_{1/3}Nb_{2/3}$)O_3-0.9Pb(ZrxTi1-x)O_3 ($0.3 \leq x \leq 0.9$) thin films were fabricated by chemical solution processing. The PMN-PZT thin films were dense and uniform. The dielectric constant of the film showed maximum values of ~1500 at x = 0.5. The films maintained 74-82% of their virgin remnant polarization after 10^{10} cycles. Above x=0.6, the gain size of thin film with various compositions was ranged from ~250 nm to ~50 nm with increasing x. The dielectric constants of the films decreased with increasing x. While the remanent polarization (P_r) of the films showed maximum values, ~28 μC/cm², at the composition of x = 0.8.

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From above results, two manuscripts entitled "Preparation and dielectric characteristics of $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-modified $0.9Pb(Zr_xTi_{1-x})O_3$ ($0.3 \leq x \leq 0.6$) thin films by chemical solution processing" and "Dielectric and electrical properties of preferentially (111) oriented Zr- rich $0.1Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ ($0.6 \leq x \leq 0.9$) thin films by chemical solution deposition" will be submitted to the Journal of Material Research for publicaltion.

Abstract Title	**PREPARATION AND DIELECTRIC PROPERTIES OI 0.1PMN-0.9PZT THIN FILMS BY CHEMICAL SOLUTION DEPOSITION**
Authors * Denotes the presenting author	**Jeong Hwan Park** **Ki Hyun Yoon**

PREPARATION AND DIELECTRIC PROPERTIES OF 0.1PMN-0.9PZT THIN FILMS BY CHEMICAL SOLUTION DEPOSITION

Ferroelectric thin films with 0.1Pb(Mg1/3Nb2/3)O3-0.9Pb(ZrxTi1-x)O3 (x=0.3~0.6) compositions have been prepared by the chemical solution process with corresponding metal alkoxides partially stabilized with acetylacetone. The PMN-PZT thin films were deposited on Pt-coated substrates by spin-coating, and crystallized at 700 oC in air. The films were nearly pure perovskite phase and preferentially (111)-oriented. The microstructure of the films was dense, uniform and rosette-free. The dielectric constant and remnant polarization (Pr) showed a maximum value at the composition of x = 0.5 and were ~1500 and ~18 uC/cm2, respectively. In addition, the PMN-PZT thin films did not show significant degradation after 10(10) cycles compared with unmodified PZT thin films.

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Above title will be presented in the Syposia D-3, Smart Materials, Devices and Sensors: Systems and Applications of the 102nd Annual Meeting and Exposition of the American Ceramic Society (April 30-May 3, 2000) in St.Louis, Missouri.